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(54) LEAD-FREE SOLDER

(57) A lead-free solder alloy substantially contains Sn and Ti, and has a temperature of a liquidus line of not greater than 400 °C. The lead-free solder alloy contains no toxic lead and has sufficient bonding strength to oxide materials such as glass and ceramics.

Description

Field of the invention

[0001] The present invention relates to lead-free solder alloys for soldering oxide materials, such as ceramics and glass, at a low temperature.

Background of the invention

[0002] As a preparation for soldering oxide materials such as ceramics and glass, a process of applying an electroplating or electroless plating, such as gold plating, copper plating, and nickel plating, on the oxide materials is widely known. However, it is expensive and complicated to solder plated surfaces. Therefore, it is desired to develop an economic solder alloy.

[0003] To comply with the aforementioned demand, Japanese patent publication 49-22299B and Japanese patent publication 52-21980B disclose Pb-Sn solder alloys which can be directly soldered to glass and ceramics.

[0004] However, lead is toxic and has been recognized as hazards to injure human health and to hurt the environment, affecting the ecosystem, so the use of lead poses a problem. The trend to use no lead in solder alloy has been rapidly increased.

[0005] The solder alloy disclosed in the above Japanese patent publication 49-22299B is a Pb-Sn-Cd-Sb solder alloy which can be directly soldered to an oxide film material such as glass and ceramics, but includes toxic lead. The lead elutes in quantity from refuse of products manufactured usin g the solder alloy so as to cause serious problem to the environment when the products are exposed to acid rain.

[0006] The solder alloy disclosed in the above Japanese patent publication 52-21980B is a solder alloy containing rare earth metals which is useful for bonding oxide materials such as glass and ceramics. However, the solder alloy has the same problems as above because it contains lead as a main component.

[0007] Development has been actively carried out to provide improved lead-free solder alloys especially for mounting electronic components to a printed wiring board. For example, a Sn-Ag-In solder alloy is disclosed in Japanese patent publication 9-326554A, and a Sn-Zn-Bi solder alloy is disclosed in Japanese patent publication 8-164495A. However, their bonding strength are not enough for oxide materials such as glass and ceramics.

[0008] As an example of lead-free solder alloys for soldering metal oxide materials, a Sn-Ag-Al-Zn solder alloy is disclosed in Japanese patent publication 55-36032B. The resultant solder layer easily separates from oxide material such as glass and ceramics because this solder alloy is for soldering metal and therefore the coefficient of thermal expansion of the solder alloy is greatly different from that of the oxide material.

Object and summary of the invention

[0009] The present invention was made taking the aforementioned prior arts into consideration and the object of the present invention is to provide lead-free solder alloys which contain no toxic lead and have sufficient bonding strength to oxide materials such as glass and ceramics.

[0010] The present invention is made to provide a solder alloy for bonding oxide materials such as glass and ceramics, wherein the solder alloy contains Ag, Cu, Zn, Al in addition to essential constituents, Sn and Ti, and further contains O wherein O content is defined. It should be noted that each composition for all of the constituents is an average composition in the solder alloy because the lead-free solder alloy of the present invention contains elements such as Zn, Ti, Al which are extremely easy to be oxidized and are easily segregate on the surface of the solder alloy.

[0011] A lead-free solder alloy of this invention is characterized by containing Sn and Ti and having a liquidus temperature equal to or less than 400 °C.

[0012] In lead-free solder alloy of the present invention, the temperature of the liquidus line is preferably not lower than 200 °C in view of long-term stability under the condition that a portion to be soldered is subjected to high temperature.

[0013] The temperature of the liquidus line means the temperature at which a lead-free solder alloy of the present invention is completely melted and can be measured by, for example, a differential scanning calorimetry (DSC).

[0014] The lead-free solder alloy of the present invention preferably contains at least 0.0001% by weight O as a constituent. More preferably, the content of O is greater than 0.01% by weight.

[0015] The lead-free solder alloy of the present invention preferably further contains from 0.1% to 6.0% by weight Ag as a constituent.

[0016] The lead-free solder alloy of the present invention preferably further contains from 0.001% to 6.0% by weight Cu as a constituent.

[0017] The lead-free solder alloy of the present invention preferably further contains from 0.001% to 1.0% by weight Ti as a constituent.

[0018] The lead-free solder alloy of the present invention preferably further contains from 0.001% to 3.0% by weight Zn as a constituent.

[0019] The lead-free solder alloy of the present invention preferably further contains from 0.001% to 3.0% by weight Al as a constituent.

[0020] The lead-free solder alloy of the present invention preferably further contains at least one element selected from a group consisting of Bi, Si, and Sb in a range not greater than 10% by weight altogether.

[0021] The lead-free solder alloy of the present invention preferably further contains from 0.001% to 1.0 % by weight Si.

[0022] The lead-free solder alloy of the present invention preferably further contains at least one trace constituent selected from a group consisting of Fe, Ni, Co, Ga, Ge, and P in a range not greater than 1.0% by weight altogether.

Preferred embodiments

[0023] The followings are reasons of employing constituents of lead-free solder alloys according to the present invention. The contents of constituents will be represented by weight percent.

[0024] Sn (tin) is not toxic and can give good wetting property on materials to be bonded so that Sn is an indispensable constituent for solder alloy. The content of Sn is preferably equal to or more than 90.0%.

[0025] Ti (titanium) is extremely easy to be oxidized, but has an advantage in facilitating bonding between oxide materials and the solder alloy. However, addition of Ti increases the liquidus temperature of the solder alloy. If the liquidus temperature exceeds 400°C, the solder alloy has poor workability. It is preferable to add Ti within a range in which the liquidus temperature of the resultant solder alloy does not exceed 400°C. When Sn is used singly as solder, there is a possibility of phase transition due to temperature change and the phase transition may be detrimental to long-term stability. By adding Ti in a suitable amount, the phase transition of the solder alloy can be prevented. The content of Ti is preferably in a range from 0.001 to 1.0%.

[0026] O (oxygen) is an indispensable constituent for lead-free solder alloy for soldering oxide materials such as ceramics and glass. By adding a suitable amount of O in the solder alloy, bonding is made on interfaces between the oxide material and the solder alloy via O, thereby increasing the bonding strength of the resultant solder layer. In this case, the content of O is preferably in a range not less than 0.0001%. More preferably, the content of O is in a range not less than 0.01%. However, when an excess amount of O is contained in the solder alloy, oxides may be undesirably produced in the resultant solder layer by the soldering process. Accordingly, the content of O is preferably in a range not greater than 1.5 %. The adjustment of the content of O in the solder alloy can be achieved by suitably selecting the concentration of oxygen in the ambient atmosphere where predetermined raw materials are melted to prepare the solder alloy and suitably selecting the melting period of time.

[0027] Ag (silver) has a good effect on improving the mechanical strength of the resultant solder alloy. When the content of Ag is less than 0.1%, such effect of improving the mechanical strength is not enough. Addition of Ag in an amount exceeding 6.0% increases the melting point of the resultant solder alloy and produces a lot of Ag-Sn intermetallic compounds, and thus, on the contrary, reduces the mechanical strength. Accordingly, the content of Ag is preferably in a range from 0.1 to 3.5%.

[0028] Cu (copper) has a good effect on improving the mechanical strength of the resultant solder alloy, as well as Ag. Addition of Cu in an amount exceeding 6.0% increases the melting point of the resultant solder alloy and produces a lot of Cu-Sn intermetallic compounds, and thus, on the contrary, reduces the mechanical strength. Accordingly, the content of Cu is preferably in a range from 0.01 to 3.0%.

[0029] Zn (Zinc) is preferably added by 0.001% or more in the solder alloy in order to improve bonding strength to oxide materials including glass and ceramics. Zn content exceeding 3.0% is not preferable in practice because the resultant solder layer may become friable.

[0030] Al (aluminum) is extremely easy to be oxidized just as Ti, but has an advantage in facilitating bond between oxide materials and the solder alloy. When the content of A1 is less than 0.001%, the aforementioned advantage is not achieved fully. Addition of A1 in an amount exceeding 3.0% increases the hardness of the resultant solder alloy and makes it difficult to ensure heat cycle resistance, and increases the melting point of the solder alloy, so that the solder alloy has poor workability. Accordingly, the content of Al is preferably in a range from 0.01 to 1.0%.

[0031] The lead-free solder alloy according to the present invention may contain one or more elements among Bi, Si and Sb in a range not greater than 10%. Bi and Si improve the wettability of the solder alloy. To add Sb improves the appearance of a soldered portion and increases creep resistance of the resultant solder layer. The solder alloy may contain further another elements such as Fe, Ni, Co, Ga, Ge, P in a trace amount to improve characteristics of

the solder alloy, such as workability and mechanical strength, besides lead-free.

[0032] Si content less than 0.001% is too small to have the effect. Si content exceeding 1.0% is too much because it increases the melting point of the solder alloy so that the solder alloy has poor workability. Accordingly, Si content is more preferably in a range from 0.01 to 0.1%.

[0033] Moreover, the lead-free solder alloy according to the present invention may optionally contain a suitable amount of In. Addition of In lowers melting point of the solder alloy, and improves wettability and flexibility of the solder alloy, thereby relaxing the stress applied to the interface between the resultant solder layer and oxide material.

[0034] Addition of a suitable amount of Fe, Ni, Co, Ga, Ge, P as trace constituent not only increases the bonding strength to glass but also improves the mechanical strength of the resultant solder layer and provides various characteristics for bonding the solder alloy and the glass firmly such as a characteristic for relaxing the distortion of the interface between the glass and the resultant solder layer when cooled, whereby the solder alloy can bond glass surfaces to each other firmly and has no problem of separation due to impact after soldered. In this case, the content of these optional constituents is preferably 1.0% or less.

The lead-free solder alloy according to the present invention can directly solder not only oxide materials such as glass and ceramics but also metals, which are difficult to be soldered because of their oxide films on their surfaces, such as aluminum, titanium, and zirconium. In case of soldering such materials, a device for applying ultrasonic vibration to the solder alloy is preferably employed.

[0035] Hereinafter, the present invention will be described referring to concrete examples.

Examples 1-10

[0036] Samples for the examples were prepared as follows. Soda-lime glass plates (50 x 50 x 3 mm) were used as materials to be solder-bonded. Lead-free solder alloys made of constituents shown in Table 1 were melted to adhere to the glass plate with using an ultrasonic soldering iron having a tip which vibrates at 60 kHz. The constituents in Table 1 are represented by weight percent.

[0037] Bonding property of each lead-free solder alloy to the glass plate was estimated according to the separation of the lead-free solder alloy caused by scraping the resultant solder layer on the glass with a knife. In Table 1, a circle mark ($_{\text{o}}$) of the bonding property shows that more than half of the resultant solder layer remains on the glass plate, and a cross mark ($_{\text{x}}$) shows that the resultant solder layer separates from the glass plate in its entirety.

Table 1.

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Example 10
Sn	99.939	99.89	95.9	99.289	90.9975	99.49	99.5	96.199	97.68	94.977
Ti	0.05	0.01	0.1	0.001	0.002	0.005	0.05	0.001	0.02	0.003
Ag	0	0	3.0	0	0	0	0.1	0	1.0	0
Cu	0.01	0	0	0.7	0	0	0.1	0	0.5	3.0
Zn	0	0	0	0	9.0	0	0.1	3.0	0.5	2.0
Al	0	0	0	0	0	0.5	0.1	0.3	0	0
O	0.001	0.1	1.0	0.01	0.0005	0.005	0.05	0.5	0.3	0.02
Total	100	100	100	100	100	100	100	100	100	100
Bonding property	○	○	○	○	○	○	○	○	○	○
Temperature of liquidus line (℃)	310	250	380	229	203	236	314	210	264	235

[0038] As apparent from Table 1, each of samples of these examples has the liquidus temperatures not greater than than 400 °C as described in claim 1, so that the lead-free solder alloy can be soldered to various oxide materials. The lead-free solder alloy contains suitable amounts of constituents according to claims 1 through 11 so as to increase bonding strength to glass, and additionally to improve various characteristics for bonding the solder alloy and the glass plate firmly, such as mechanical strength of the resultant solder layer and an ability of relaxing the distortion of the interface between the glass plate and the resultant solder layer when cooled, whereby the solder alloy can bond glass plates to each other firmly and has no problem of separation due to impact after soldered.

Comparative Examples 1 and 2

[0039] Samples for the comparative examples were prepared as follows. Soda-lime glass plates (50 x 50 x 3 mm) were used as materials to be solder-bonded. Lead-free solder alloys made of constituents shown in Table 2 were melted to adhere to the glass plate with using the ultrasonic soldering iron having a tip which vibrates at 60 kHz. The constituents in Table 2 are represented by weight percent.

[0040] Bonding property of each solder alloy to the glass plate was estimated according to the separation of the lead-free solder alloy caused by scraping the resultant solder layer on the glass with a knife in the same manner as the cases of Examples 1-10. In Table 2, a circle mark (o) of the bonding property shows that more than half of the resultant solder layer remains on the glass plate, and a cross mark (x) shows that the resultant solder layer separates from the glass plate in its entirety.

Table 2.

	Comparative Example 1	Comparative Example 2
Sn	96.4	99.2
Ti	0	0
Ag	3.5	0
Cu	0	0.7
Zn	0	0
Al	0	0
O	0.1	0.1
Total	100	100
Bonding property	x	x
Temperature of liquidus line (°C)	221	227

[0041] In both comparative example 1 and comparative example 2 shown in Table 2, the content of Ti is out of the scope of the present invention. Therefore, the lead-free solder alloys of the comparative examples have poor bonding strength to the glass plate so that both of the resultant solder layers separate from the glass plates in its entirety.

Examples 11 - 20

[0042] Samples for the examples were prepared as follows. Soda-lime glass plates (50 x 50 x 3 mm) were used as materials to be solder-bonded. Lead-free solder alloys made of constituents shown in Table 3 were melted to adhere to the glass plate with using the ultrasonic soldering iron having a tip which vibrates at 60 kHz. The constituents in Table are represented by weight percent.

[0043] Bonding property of each solder alloy to the glass plate was estimated according to the separation of the lead-free solder alloy caused by scraping the resultant solder layer on the glass with a knife in the same manner as the cases of Examples 1-10. In Table 3, a circle mark (o) of the bonding property shows that more than half of the resultant solder layer remains on the glass plate, and a cross mark (x) shows that the resultant solder layer separates in its entirety.

Table 3.

	Example 11	Example 12	Example 13	Example 14	Example 15	Example 16	Example 17	Example 18	Example 19	Example 20
Sn	94.939	94.89	95.89	93.289	90.9965	99.489	99.499	96.198	97.679	94.976
Ti	0.05	0.01	0.1	0.001	0.002	0.005	0.05	0.001	0.02	0.003
Ag	0	0	3.0	0	0	0	0.1	0	1.0	0
Cu	0.01	0	0	0.7	0	0	0.1	0	0.5	3.0
Zn	0	0	0	0	9.0	0	0.1	3.0	0.5	2.0
Al	0	0	0	0	0	0.5	0.1	0.3	0	0
O	0.001	0.1	1.0	0.01	0.0005	0.005	0.05	0.5	0.3	0.02
Sb	5	0	0	3	0	0	0	0	0	0
Si	0	0	0.01	0	0	0	0	0	0	0
Bi	0	5	0	3	0	0	0	0	0	0
Fe	0	0	0	0	0.001	0	0	0	0	0
Ni	0	0	0	0	0	0.001	0	0	0	0
Co	0	0	0	0	0	0	0.001	0	0	0
Ga	0	0	0	0	0	0	0	0.001	0	0
Ge	0	0	0	0	0	0	0	0	0.001	0
P	0	0	0	0	0	0	0	0	0	0.001
Total	100	100	100	100	100	100	100	100	100	100
Bonding property	○	○	○	○	○	○	○	○	○	○
Temperature of liquidus line (℃)	315	245	390	230	203	236	314	210	264	235

[0044] As apparent from Table 3, the lead-free solder alloy of the samples contain the constituents according to claims 1 through 11, suitable amounts of additional constituents according to claims 12 and 13, and suitable amounts of Fe, Ni, Co, Ga, Ge, P as additional small constituents according to claim 14 so as to increase bonding strength and additionally improve various characteristics for bonding the solder alloy and the glass plate firmly, such as mechanical strength of the resultant solder layer and an ability of relaxing the distortion of the interface between the glass and the resultant solder layer when cooled, whereby the solder alloy can bond glass plates to each other firmly and has no problem of separation due to impact after soldered.

Industrial Applicability

[0045] As described above, the lead-free solder alloy of the present invention contains no toxic lead, and has a liquidus temperature not greater than 400 °C as described in claim 1, so that the lead-free solder alloy can be easily soldered to various oxide materials. And the lead-free solder alloy of the present invention suitably contains constituents according to claims 1 through 11, additional constituents according to claims 12 and 13, and suitable amounts of Fe, Ni, Co, Ga, Ge, P as additional trace constituents according to claim 14 so as to increase bonding strength to glass, and additionally to improve various characteristics for bonding the solder alloy and oxide materials including glass firmly, such as mechanical strength itself and an ability of relaxing the distortion of the interface between a glass surface and the solder alloy when cooled, whereby the solder alloy can bond oxide materials including glass and ceramics to each other firmly and is hard to separate after soldered.

Claims

1. A lead-free solder alloy substantially containing Sn and Ti and having a liquidus temperature not greater than 400 °C.

2. A lead-free solder alloy as claimed in claim 1, wherein said lead-free solder alloy further contains at least 0.0001% by weight O.

3. A lead-free solder alloy as claimed in claim 2, wherein the content of O is equal to or more than 0.01% by weight.

4. A lead-free solder alloy as claimed in claim 3, wherein the content of O is in a range from 0.01 to 1.5% by weight.

5. A lead-free solder alloy as claimed in any one of claims 1 through 4, wherein the temperature of the liquidus line is not lower than 200 °C.

6. A lead-free solder alloy as claimed in any one of claims 1 through 5, wherein Sn content is equal to or more than 90.0% by weight.

7. A lead-free solder alloy as claimed in any one of claims 1 through 6, wherein Ti content is in a range from 0.001% to 1.0% by weight.

8. A lead-free solder alloy as claimed in any one of claims 1 through 7, wherein said lead-free solder alloy further contains from 0.1% to 6.0% by weight Ag..

9. A lead-free solder alloy as claimed in any one of claims 1 through 8, wherein said lead-free solder alloy further contains from 0.001% to 6.0% by weight Cu.

10. A lead-free solder alloy as claimed in any one of claims 1 through 9, wherein said lead-free solder alloy further contains from 0.001% to 3.0% by weight Zn.

11. A lead-free solder alloy as claimed in any one of claims 1 through 10, wherein said lead-free solder alloy further contains from 0.001% to 3.0% by weight Al.

12. A lead-free solder alloy as claimed in any one of claims 1 through 11, wherein said lead-free solder alloy further contains at least one element selected from a group consisting of Bi, Si, and Sb in a range not greater than 10% by weight altogether.

13. A lead-free solder alloy as claimed in any one of claims 1 through 12, wherein said lead-free solder alloy

further contains from 0.001% to 1.0 % by weight Si.

14. A lead-free solder alloy as claimed in any one of claims 1 through 13, wherein said lead-free solder alloy further contains at least one trace constituent selected from a group consisting of Fe, Ni, Co, Ga, Ge, and P in a range not greater than 1.0% by weight altogether.

15. A lead-free solder alloy as claimed in any one of claim 1 through 7, wherein said solder alloy contains Ti and O, and the balance of said solder alloy is substantially Sn.

16. A lead-free solder alloy as claimed in any one of claim 1 through 11, wherein said solder alloy contains Ti, O, and at least one element of a group consisting of Ag, Cu, Zn and Al, and the balance of said solder alloy is substantially Sn.

17. A lead-free solder alloy as claimed in any one of claim 1 through 13, wherein said solder alloy contains Ti, O, at least one element selected from a group consisting of Ag, Cu, Zn and Al, and at least one element selected from a group consisting of Bi, Si and Sb, and the balance of said solder alloy is substantially Sn.

18. A lead-free solder alloy as claimed in any one of claim 1 through 14, wherein said solder alloy contains Ti, O, at least one element selected from a group consisting of Ag, Cu, Zn and Al, at least one element selected from a group consisting of Bi, Si and Sb, and at least one of said trace constituents, and the balance of said solder alloy is substantially Sn.

Amended claims under Article 19.1 PCT.

1. (amended) A lead-free solder alloy substantially containing Sn and Ti, and having a liquidus temperature not greater than 400 °C, and further containing at least 0.0001% by weight O.

2. (amended) A lead-free solder alloy as claimed in claim 1, wherein the content of O is equal to or more than 0.01% by weight.

3. (amended) A lead-free solder alloy as claimed in claim 2, wherein the content of O is in a range from 0.01 to 1.5% by weight.

4. (amended) A lead-free solder alloy as claimed in any one of claims 1 through 3, wherein the temperature of the liquidus line is not lower than 200 °C.

5. (amended) A lead-free solder alloy as claimed in any one of claims 1 through 4, wherein Sn content is equal to or more than 90.0% by weight.

6. (amended) A lead-free solder alloy as claimed in any one of claims 1 through 5, wherein Ti content is in a range from 0.001% to 1.0% by weight.

7. (amended) A lead-free solder alloy as claimed in any one of claims 1 through 6, wherein said lead-free solder alloy further contains from 0.1% to 6.0% by weight Ag.

8. (amended) A lead-free solder alloy as claimed in any one of claims 1 through 7, wherein said lead-free solder alloy further contains from 0.001% to 6.0% by weight Cu.

9. (amended) A lead-free solder alloy as claimed in any one of claims 1 through 8, wherein said lead-free solder alloy further contains from 0.001% to 3.0% by weight Zn.

10. (amended) A lead-free solder alloy as claimed in any one of claims 1 through 9, wherein said lead-free solder alloy further contains from 0.001% to 3.0% by weight Al.

11. (amended) A lead-free solder alloy as claimed in any one of claims 1 through 10, wherein said lead-free solder alloy further contains at least one element selected from a group consisting of Bi, Si, and Sb in a range not greater than 10% by weight altogether.

12. (amended) A lead-free solder alloy as claimed in any one of claims 1 through 11, wherein said lead-free

solder alloy further contains from 0.001% to 1.0 % by weight Si.

13. (amended) A lead-free solder alloy as claimed in any one of claims 1 through 12, wherein said lead-free solder alloy further contains at least one trace constituent selected from a group consisting of Fe, Ni, Co, Ga, Ge, and P in a range not greater than 1.0% by weight altogether.

14. (amended) A lead-free solder alloy as claimed in any one of claim 1 through 6, wherein said solder alloy contains Ti and O, and the balance of said solder alloy is substantially Sn.

15. (amended) A lead-free solder alloy as claimed in any one of claim 1 through 10, wherein said solder alloy contains Ti, O, and at least one element of a group consisting of Ag, Cu, Zn and Al, and the balance of said solder alloy is substantially Sn.

16. (amended) A lead-free solder alloy as claimed in any one of claim 1 through 12, wherein said solder alloy contains Ti, O, at least one element selected from a group consisting of Ag, Cu, Zn and Al, and at least one element selected from a group consisting of Bi, Si and Sb, and the balance of said solder alloy is substantially Sn.

17. (amended) A lead-free solder alloy as claimed in any one of claim 1 through 13, wherein said solder alloy contains Ti, O, at least one element selected from a group consisting of Ag, Cu, Zn and Al, at least one element selected from a group consisting of Bi, Si and Sb, and at least one of said trace constituents, and the balance of said solder alloy is substantially Sn.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP00/03631

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl[7] B23K35/26, C22C13/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl[7] B23K35/26, B23K35/28, B23K35/30, B23K35/32
C22C13/00, C22C13/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-2000
Kokai Jitsuyo Shinan Koho 1971-2000 Jitsuyo Shinan Toroku Koho 1996-2000

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
JOIS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, 11-77370, A (Central Glass Co., Ltd.), 23 March, 1999 (23.03.99), Claim 1; Column 2, lines 42 to 46 (Family: none)	1,5,7
A	JP, 1-95893, A (Seiko Instr. Inc.), 13 April, 1989 (13.04.89), Claims 1 to 2 (Family: none)	1-18
A	JP, 2-179386, A (Tokuriki Honten Co., Ltd.), 12 July, 1990 (12.07.90), Claim 1 (Family: none)	1-18
A	JP, 4-305073, A (Tanaka Kikinzoku Kogyo K.K.), 28 October, 1992 (28.10.92), Claim 1 (Family: none)	1-18
A	JP, 64-71592, A (Nippon Kogaku K.K.), 16 March, 1989 (16.03.89), Claims 1 to 2 (Family: none)	1-18
A	JP, 53-124148, A (Seiko Epson Corporation), 30 October, 1978 (30.10.78),	1-18

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
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Date of the actual completion of the international search
28 August, 2000 (28.08.00)

Date of mailing of the international search report
05 September, 2000 (05.09.00)

Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP00/03631

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Claims 1 to 4 (Family: none)	
A	JP, 64-18981, A (Hitachi, Ltd.), 23 January, 1989 (23.01.89), page 2, upper right column lines 5 to 8 (Family: none)	1-18

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